05 - Chemical reaction systems

Mass action type kinetic differential equations

Let us consider a vessel (a cell, a reactor, a test tube etc.) of constant volume at constant pressure and temperature where chemical reactions take place between some chemical species (atoms, ions or molecules). Let $M,\ R \in \mathbb{N};\ \alpha,\ \beta \in \mathbb{N}_0^{M\times R};\ k_r \in \mathbb{R}^+$ and consider the **complex chemical reaction**:

$$\sum_{m=1}^{M} \alpha(m,r)\,X(m) \xrightarrow{k_r} \sum_{m=1}^{M} \beta(m,r)\,X(m) \qquad (r = 1, 2, \ldots, R) \qquad (1)$$

where the meaning of the notations is the following:

M denotes the number of chemical species;
$X(m)$ denotes the mth chemical species ($m = 1, 2, \ldots, M$);
R denotes the number of reaction steps;
$\alpha(m, r)$ and $\beta(m, r)$ denote the reactant and product stoichiometric coefficients;
k_r denotes the reaction rate coefficients.

Suppose the reaction can adequately be described using **mass action kinetics**, then its **deterministic model** is

$$c_m'(t) = f_m(\mathbf{c}(t)) := \sum_{r=1}^{R} (\beta(m,r) - \alpha(m,r))\, k_r \prod_{p=1}^{M} c_p(t)^{\alpha(p,r)} \qquad (2)$$

$$c_m(0) = c_{m_0} \in \mathbb{R}_0^+ \ (m = 1, 2, \ldots, M) \qquad (3)$$

describing the time evolution of the concentration vs. time functions $t \mapsto c_m(t) := [X(m)](t)$ of the species. Equation (2) is also called the mass action type **induced kinetic differential equation** of the reaction (1).

Examples

Example 1. $2X + Y \xrightarrow{a} 2Z,\ 2Z \xrightarrow{b} 2X + Y$

$$x' = (0-2)\,a\,x^2 y^1 z^0 + (2-0)\,b\,x^0 y^0 z^2 = -2\,a\,x^2 y + 2\,b\,z^2$$
$$y' = (0-1)\,a\,x^2 y^1 z^0 + (1-0)\,b\,x^0 y^0 z^2 = -a\,x^2 y + b\,z^2$$
$$z' = (2-0)\,a\,x^2 y^1 z^0 + (0-2)\,b\,x^0 y^0 z^2 = 2\,a\,x^2 y - 2\,b\,z^2$$

Example 2. $X \xrightarrow{a} Y,\ Y \xrightarrow{b} Z,\ Z \xrightarrow{c} X$

$$x' = -a\,x + c\,z$$
$$y' = a\,x - b\,y$$
$$z' = b\,y - c\,z$$

Example 3. Finding a chemical reaction to a given differential equation system is usually not unique, for example:

$$x' = 2x + 3y \qquad \text{Possible reactions: } X \xrightarrow{4} X + Y \xleftarrow{3} Y,\quad Y \xrightarrow{1} 0,\quad X \xrightarrow{2} 2X$$
$$y' = 4x - y \qquad X \xrightarrow{4} X + Y \xleftarrow{3} Y,\quad Y \xrightarrow{1} 0,\quad X \xrightarrow{1} 3X$$

Negative cross effect

The induced kinetic differential equation of the reaction (1) is a polynomial differential equation since all the functions f_m are polynomials in all their variables. However, it is not true that all polynomial differential equations can be obtained as induced kinetic differential equations of some reactions, as the following examples show.

1) The model of the harmonic oscillator: $x' = y$

$$y' = \boxed{-x}$$

2) The Lorenz model: $x' = \sigma(y - x)$ $(\sigma, \varrho, \beta > 0)$

$$y' = \varrho x \boxed{-xz}$$
$$z' = xy - \beta z$$

The speciality of kinetic differential equations is that they cannot contain terms like those boxed above, i.e. terms expressing the decay of a quantity without its participation. Such terms are said to represent **negative cross effects**. Moreover, it is also true that the absence of such terms allows us to construct a reaction inducing the given differential equation.

Examples

Example 1. First-order decay reaction: $X \xrightarrow{k} Y$

(1) $x'(t) = -k\,x(t) \qquad x(0) = x_0 > 0$

(2) $y'(t) = k\,x(t) \qquad y(0) = y_0 \geq 0 \qquad (k > 0,\ t \geq 0)$

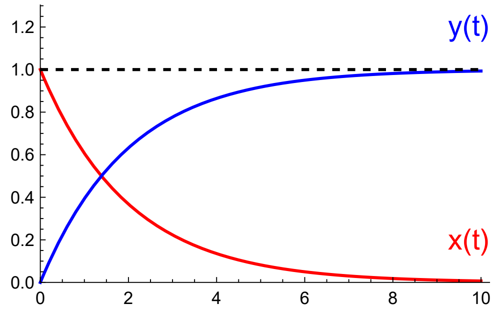
Solution. Equation (1) is separable, the solution is $x(t) = x_0\, e^{-k t}$.

Since $x'(t) + y'(t) = 0 \implies x(t) + y(t) = x_0 + y_0$ for all $t \geq 0$

$\implies y(t) = x_0 + y_0 - x(t) = x_0 + y_0 - x_0\, e^{-k t}$.

Limits at infinity: $\lim_{t\to\infty} x(t) = 0$ and $\lim_{t\to\infty} y(t) = x_0 + y_0$

Plotting the solutions if $x_0 = 1,\ y_0 = 0,\ k = 0.5$:



Example 2. nth-order decay reaction: $X \xrightarrow{k} Y$

$$(1)\; x'(t) = -k\, x^n(t) \qquad x(0) = x_0 > 0$$
$$(2)\; y'(t) = k\, x^n(t) \qquad y(0) = y_0 \geq 0$$

($k > 0$ and the integer $n > 1$ is the order of the decay; $t \geq 0$)

Solution. Equation (1) is separable:

$$\frac{dx}{dt} = -k\, x^n \implies \int \frac{1}{x^n}\, dx = \int -k\, dt \implies \frac{x^{-n+1}}{-n+1} = -k\, t + c \implies$$

the solution is

$$x(t) = ((n-1)(k\, t - c))^{\frac{1}{1-n}}$$

and from the initial condition $x(0) = x_0$ we get that $c = \frac{x_0^{1-n}}{1-n}$.

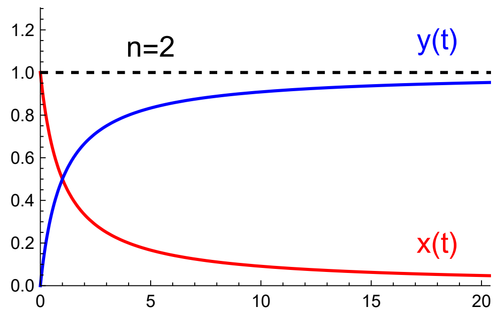
Since $x'(t) + y'(t) = 0 \implies x(t) + y(t) = x_0 + y_0$ for all $t \geq 0$

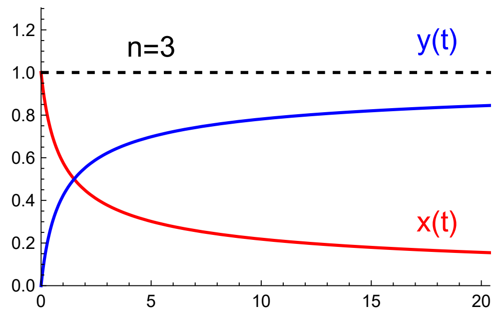
$\implies y(t) = x_0 + y_0 - x(t)$.

Limits at infinity: $\lim_{t \to \infty} x(t) = 0$ and $\lim_{t \to \infty} y(t) = x_0 + y_0$

If $n = 2$, $k = 1$, $x_0 = 1$, $y_0 = 0$ then the solution is $x(t) = \frac{1}{1+t}$, $y(t) = 1 - \frac{1}{1+t} = \frac{t}{1+t}$

If $n = 3$, $k = 1$, $x_0 = 1$, $y_0 = 0$ then the solution is $x(t) = \frac{1}{\sqrt{1+2\,t}}$, $y(t) = 1 - \frac{1}{\sqrt{1+2\,t}}$





Example 3. First-order consecutive reaction: $X \xrightarrow{k} Y \xrightarrow{m} Z$

(1) $x'(t) = -k\,x(t)$ $\quad x(0) = x_0 > 0$ $\quad (k > 0,\ m > 0,\ t \geq 0)$

(2) $y'(t) = k\,x(t) - m\,y(t)$ $\quad y(0) = y_0 \geq 0$

(3) $z'(t) = m\,y(t)$ $\quad z(0) = z_0 \geq 0$

Solution. Since $x'(t) + y'(t) + z'(t) = 0 \implies x(t) + y(t) + z(t) = x_0 + y_0 + z_0$ for all $t \geq 0$.

We solve it in the case when $x_0 = 1,\ y_0 = 0,\ z_0 = 0$.

Equation (1) is separable: $x(t) = e^{-k\,t}$.

Substituting into (2), we get a first-order linear nonhomogeneous equation (with constant coefficients):

$$y'(t) + m\,y(t) = k\,e^{-k\,t}$$

It can be solved with the variation of the constant method (see exercise 03/7)

Here we solve it with the method of undetermined coefficients.

1st step:

Homogeneous equation: $y'(t) + m\,y(t) = 0$

Characteristic equation: $\lambda + m = 0 \implies \lambda = -m$

General solution of the homogeneous equation: $y_h(t) = C\,e^{-m\,t}$

2nd step:

Finding the particular solution of the nonhomogeneous equation:

Case 1.

If $k = m \implies y_p(t) = A\,t\,e^{-k\,t}$ (outer resonance)

Substituting into (2) $\implies \left(A\,e^{-k\,t} - k\,A\,t\,e^{-k\,t}\right) + k\,A\,t\,e^{-k\,t} = k\,e^{-k\,t}$

$\implies A\,e^{-k\,t} = k\,e^{-k\,t} \implies A = k \implies y_p(t) = k\,t\,e^{-k\,t}$

General solution of the nonhomogeneous equation:

$y(t) = y_h(t) + y_p(t) = C\,e^{-m\,t} + k\,t\,e^{-k\,t}$

Initial condition: $y(0) = 0 \implies C = 0$

Solution of the initial value problem: $y(t) = k\,t\,e^{-k\,t}$

Case 2.

If $k \neq m \implies y_p(t) = A\,e^{-k\,t}$

Substituting into (2) $\implies -k\,A\,e^{-k\,t} + m\,A\,e^{-k\,t} = k\,e^{-k\,t}$

$\implies -k\,A + m\,A = k \implies A = \dfrac{k}{m-k} \implies y_p(t) = \dfrac{k}{m-k}\,e^{-k\,t}$

General solution of the nonhomogeneous equation:

$$y(t) = y_h(t) + y_p(t) = C\,e^{-m\,t} + \frac{k}{m-k}\,e^{-k\,t}$$

Initial condition: $y(0) = 0 \implies C + \dfrac{k}{m-k} = 0 \implies C = \dfrac{k}{k-m}$

Solution of the initial value problem:

$$y(t) = \frac{k}{k-m}\,e^{-m\,t} - \frac{k}{k-m}\,e^{-k\,t}$$

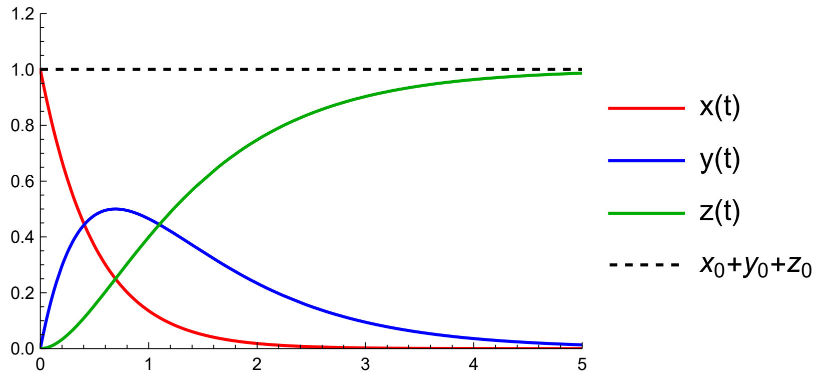
Substituting into (3), we get a directly integrable equation for $z(t)$. Or:

$$z(t) = x_0 + y_0 + z_0 - x(t) - y(t) = 1 - e^{-k\,t} - \frac{k}{k-m}\left(e^{-m\,t} - e^{-k\,t}\right)$$

$$z(t) = 1 - \frac{k}{k-m} e^{-m t} + \frac{m}{k-m} e^{-k t}$$

Limits at infinity: $\lim_{t\to\infty} x(t) = 0$, $\lim_{t\to\infty} y(t) = 0$, $\lim_{t\to\infty} z(t) = 1$

Plotting the solutions if $x_0 = 1,\ y_0 = 0,\ z_0 = 0,\ k = 2,\ m = 1$:



Example 4. First-order reversible decay reaction: $X \underset{m}{\overset{k}{\rightleftharpoons}} Y$

$$x'(t) = -k\,x(t) + m\,y(t) \qquad x(0) = x_0 > 0$$
$$y'(t) = k\,x(t) - m\,y(t) \qquad y(0) = y_0 > 0$$

Solution. Since $x'(t) + y'(t) = 0 \implies x(t) + y(t) = x_0 + y_0$ for all $t \geq 0$

$\implies y(t) = x_0 + y_0 - x(t)$

$\implies x'(t) = -k\,x(t) + m(x_0 + y_0 - x(t))$

$x'(t) = -(k+m)\,x(t) + m(x_0 + y_0)$

$x'(t) = -A\,x(t) + B$ where $A = k + m,\ B = m(x_0 + y_0)$

This is a first-order linear nonhomogeneous equation.

Solution of the homogeneous equation: $x_h(t) = c \cdot e^{-A t}$

Particular solution of the nonhomogeneous equation: $x_p(t) = \frac{B}{A}$

General solution: $x(t) = x_h(t) + x_p(t) = c \cdot e^{-A t} + \frac{B}{A}$

Solution of the initial value problem: $x(t) = \left(x_0 - \frac{B}{A}\right) e^{-A t} + \frac{B}{A}$

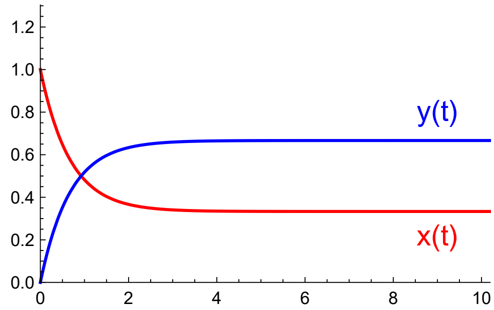
Substituting A and B: $x(t) = \frac{k\,x_0 - m\,y_0}{k+m} e^{-(k+m)\,t} + \frac{m(x_0 + y_0)}{k+m}$

$$y(t) = x_0 + y_0 - x(t) = -\frac{k\,x_0 - m\,y_0}{k+m} e^{-(k+m)\,t} + \frac{k(x_0 + y_0)}{k+m}$$

Limits at infinity:

$\lim_{t\to\infty} x(t) = \frac{m(x_0 + y_0)}{k+m}$, $\lim_{t\to\infty} y(t) = \frac{k(x_0 + y_0)}{k+m}$ and $\lim_{t\to\infty} \frac{x(t)}{y(t)} = \frac{m}{k}$

Plotting the solutions if $x_0 = 1,\ y_0 = 0,\ k = 1,\ m = 0.5$:



Example 5. Second-order reaction: $X + Y \xrightarrow{k} Z$

$$x'(t) = -k\,x(t)\,y(t) \qquad x(0) = x_0 > 0$$
$$y'(t) = -k\,x(t)\,y(t) \qquad y(0) = y_0 > 0$$
$$z'(t) = k\,x(t)\,y(t) \qquad z(t) = z_0 \geq 0$$

Solution. Assume that $x_0 > y_0$ and let $M = x_0 - y_0 > 0$.

Since $x'(t) - y'(t) = 0 \implies x(t) - y(t) = x_0 - y_0 = M$ for all $t \geq 0$

$\implies y(t) = x(t) - M$

$\implies x'(t) = -k\,x(t)\,(x(t) - M)$

$\implies x'(t) = k\,x(t)\,(M - x(t))$

This is a first-order separable equation for $x(t)$, where $x(t) > M$, see the solution of the logistic population model.

$$\int \frac{1}{x(M-x)}\,dx = \int k\,dt$$

Partial fraction decomposition: $\int \left(\frac{1}{M} \cdot \frac{1}{x} + \frac{1}{M} \cdot \frac{1}{(M-x)}\right) dx = \int k\,dt$

The general solution in an implicit form:

$$\frac{1}{M} \ln |x| - \frac{1}{M} \ln |M - x| = k\,t + c_1$$

From here $x(t)$ can be expressed:

$$x(t) = \frac{M\,C\,e^{M k t}}{1 + C\,e^{M k t}}, \quad C \in \mathbb{R}$$

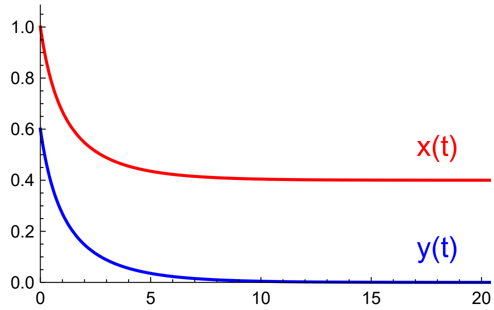
From the initial condition: $x(0) = x_0 = \frac{M\,C}{1 + C} \implies C = \frac{x_0}{M - x_0} = -\frac{x_0}{y_0}$

The solution of the initial value problem is:

$$x(t) = \frac{x_0(x_0 - y_0)}{x_0 - y_0\,e^{-(x_0 - y_0)\,k\,t}}, \quad y(t) = \frac{x_0(x_0 - y_0)}{x_0 - y_0\,e^{-(x_0 - y_0)\,k\,t}} - (x_0 - y_0)$$

Limits at infinity: $\lim_{t \to \infty} x(t) = \frac{x_0(x_0 - y_0)}{x_0 - 0} = x_0 - y_0 > 0, \ \lim_{t \to \infty} y(t) = 0.$

Plotting the solutions if $k = 1$, $x_0 = 1$, $y_0 = 0.6$:



Example 6. Autocatalytic reaction: $X + 2\,Y \xrightarrow{k} 3\,Y$

$$x'(t) = -k\,x(t)\,y^2(t) \qquad x(0) = x_0 > 0$$
$$y'(t) = k\,x(t)\,y^2(t) \qquad y(0) = y_0 > 0$$

Solution. Since $x'(t) + y'(t) = 0 \implies x(t) + y(t) = x_0 + y_0$ for all $t \geq 0$. Let $x_0 + y_0 = M$

$\implies x'(t) = -k\,x(t)\,(M - x(t))^2$

This is a first-order separable equation for $x(t)$, where $0 < x(t) < M$.

$$\implies \int \frac{1}{x(M-x)^2}\,\mathrm{dx} = \int -k\,\mathrm{dt}$$

Partial fraction decomposition: $\frac{1}{x(M-x)^2} = \frac{1}{x(x-M)^2} = \frac{A}{x} + \frac{B}{x-M} + \frac{C}{(x-M)^2}$

$$\implies \frac{1}{x(M-x)^2} = \frac{1}{M^2}\left(\frac{1}{x} - \frac{1}{x-M} + \frac{M}{(x-M)^2}\right)$$

The general solution in an implicit form:

$$\frac{1}{M^2}\left(\ln\left|x\right| - \ln\left|x-M\right| - \frac{M}{x-M}\right) = -k\,t + c_1$$

From here $x(t)$ cannot be expressed.

Limits at infinity: $\lim_{t\to\infty} x(t) = 0, \quad \lim_{t\to\infty} y(t) = x_0 + y_0$

Plotting the solutions if $k = 0.2$, $x_0 = 2$, $y_0 = 1$: